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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
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09/296,835

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RONALD A. WEIMER

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DICKSTEIN SHAPIRO MORIN & OSHINSKY LLP
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EXAMINER

KIELIN, ERIK J

ART UNIT

PAPER NUMBER

2813

DATE MAILED: 08/12/2002

31

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary

Application No.

09/296,835

Applicant(s)

WEIMER ET AL.

Examiner

Erik Kielin

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-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133).
- Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 30 May 2002.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 2-5, 8, 10-12 and 41-44 is/are pending in the application.
- 4a) Of the above claim(s) 41 is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 2-5, 8, 10-12 and 42-44 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
- Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
- 11) ☐ The proposed drawing correction filed on _____ is: a) ☐ approved b) ☐ disapproved by the Examiner.
- If approved, corrected drawings are required in reply to this Office action.
- 12) ☐ The oath or declaration is objected to by the Examiner.

Priority under 35 U.S.C. §§ 119 and 120

- 13) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. _____.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
- * See the attached detailed Office action for a list of the certified copies not received.
- 14) ☐ Acknowledgment is made of a claim for domestic priority under 35 U.S.C. § 119(e) (to a provisional application).
- a) ☐ The translation of the foreign language provisional application has been received.
- 15) ☐ Acknowledgment is made of a claim for domestic priority under 35 U.S.C. §§ 120 and/or 121.

Attachment(s)

- 1) ☒ Notice of References Cited (PTO-892)
- 2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
- 3) ☒ Information Disclosure Statement(s) (PTO-1449) Paper No(s) 29.
- 4) ☐ Interview Summary (PTO-413) Paper No(s). _____
- 5) ☐ Notice of Informal Patent Application (PTO-152)
- 6) ☐ Other:

DETAILED ACTION

Election/Restrictions

1. Applicant's election with traverse of the invention of group II, claims 2-5, 8, 10-12, and 42-44 in Paper No. 30 is acknowledged. The traversal is on the ground(s) that (1) search the patentably distinct inventions would not impose undue burden on Examiner to search and examine and (2) that silicon nitride is "an oxygen-deficient dielectric film with a high dielectric constant." Regarding (1), this is not found persuasive because undue burden of search has already been established by the different classifications. Regarding (1), this is not found persuasive because Applicant contradicts himself with the statement that silicon nitride is "an oxygen-deficient dielectric film with a high dielectric constant." Applicant's specification indicates, at p. 1, lines 24-25 and p. 3, lines 4-6, that a high dielectric constant material is one with a dielectric constant at least about 25. Silicon nitride has a dielectric constant of from 6 to 9, and therefore does not qualify as a high dielectric constant material by Applicant's own definition. (See **Wolf**, et al. Silicon Processing for the VLSI Era, Vol. 1-Process Technology, 2nd ed., Lattice Press: Sunset Beach CA, 1986, pp. 191-192 --especially Table 3.) Moreover, Applicant intends to add oxygen to the "oxygen-deficient" silicon nitride thereby converting it to silicon oxynitride, which **Wolf** makes clear will necessarily have an even *lower* dielectric constant than silicon nitride because silicon oxide has a dielectric constant of about 4.2 and silicon oxynitride will have a dielectric constant between that of silicon nitride and silicon oxide, based upon the relative amounts of nitrogen and oxygen in the silicon oxynitride. Accordingly,

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Applicant's argument that silicon nitride is even remotely related to the other high dielectric constant materials is moot based upon Applicant's own specification.

The requirement is still deemed proper and is therefore made FINAL.

Claim Rejections - 35 USC § 112

2. Claim 44 is rejected under 35 U.S.C. 112, first paragraph, as containing subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

Applicant's specification does not provide support for the combination of providing steam both by using "a wet oxidation with steam provided by a mixture of hydrogen and oxygen gases" along with steam provided by a bubbled water vapor system. Instead, the specification provides only for the sources separately.

Claim Rejections - 35 USC § 103

3. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

4. Claims 8, 2-5, 10-12 are rejected under 35 U.S.C. 103(a) as being unpatentable over Patel et al. (US 5,374,578) in view of either of Emesh et al. (US 5,728,603) and Chivukula et al. (US 6,066,581), and further in view of the excerpt from Van Zant, (Microchip Fabrication, A

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Practical Guide to Semiconductor Processing, 3rd ed. McGraw-Hill: New York, 1997, pp. 157-160).

Regarding independent claim 8, **Patel** discloses a method of forming a semiconductor device comprising,

forming an oxygen deficient dielectric (called "ferroelectric") film **14** (Figs. 2-6) such as PZT which inherently has a dielectric constant of greater than 25 (see **Emesh** col. 8, Table 1 who teaches the dielectric of PZT the same ferroelectric in **Patel**);

subjecting the dielectric film to an oxidation in "[g]ases like oxygen, ozone or air" (column 4, lines 10-11) using RTA (rapid thermal annealing), which must necessarily occur, then, in an RTA chamber, as further limited by instant claim 12 at a temperature range of 650-850 °C for about 5-30 seconds (as further limited by instant claims 2-4) in order to increase the oxygen content of the ferroelectric film (column 2, lines 30-33); and

performing a stabilizing treatment using oxygen anneal either before or after the ozone anneal (column 4, lines 23-29), as further limited by instant claim 10.

Patel does not teach using wet oxidation to anneal the ferroelectric PZT layer **14**.

Emesh teaches forming an oxygen deficient ferroelectric material such as PZT; subjecting the dielectric film to a wet oxidation using a mixture comprising water and ozone in a rapid thermal annealing (RTA) chamber in order to reduce the temperature at which the ferroelectric material densifies/crystallizes and also to reduce the stress in the ferroelectric film and improves its the electrical properties (column 5, lines 50-67) which also inherently increases the oxygen content of the film as indicated by reduced leakage current (sentence bridging columns 3-4).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to incorporate water during the ozone anneal of **Patel** for the reasons indicated in **Emesh** which includes at least reducing the stress in the ferroelectric film and improving the electrical properties such as increased dielectric constant (column 5, lines 50-67; col. 8, Table 1).

Similarly, **Chivukula** teaches forming an oxygen deficient ferroelectric material such as PZT; subjecting the dielectric film to a wet oxidation using a mixture comprising water and ozone at a temperature of 450-650 °C in a rapid thermal annealing (RTA) chamber for 30 seconds to several minutes to form uniform grain sizes in the ferroelectric material in a shorter time, at reduced temperature and superior characteristics during high frequency use compared to using dry oxidation (column 14, lines 27-48). (See also column 13, lines 30-53.)

It would have been obvious to one of ordinary skill in the art at the time the invention was made to incorporate water during the ozone anneal of **Patel** for the reasons indicated in **Chivukula**, as noted.

Patel in view of either of **Emesh** and **Chivukula** further does not teach that the steam is provided by using a mixture of hydrogen and oxygen. Instead, each of **Emesh** and **Chivukula** use a bubbler (**Emesh** at col. 5, lines 57-59; **Chivukula** at col. 13, lines 40-46).

Van Zant teaches that "Dryox," a mixture of hydrogen and oxygen which react to form a steam oxidizing mixture in the reactor, is preferred over liquid systems such as a bubbler, because the process is cleaner and more controllable and also that "Dryox is the preferred method for production of advanced devices." (See pp. 157-160 -- especially page 160.)

It would have been obvious to one of ordinary skill in the art at the time the invention was made to use hydrogen and oxygen as taught by **Van Zant** to form the steam for the wet

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oxidation mixture of either of **Emesh** and **Chivukula**, for the reasons indicated in **Van Zant**, as noted and especially because “Dryox” is preferred to bubblers which **Emesh** and **Chivukula** use.

Furthermore, it would be a matter of design choice as to which method of introducing the water to the oxidizing atmosphere of **Patel** in view of **Emesh** and **Chivukula**, because it appears that any known method of providing steam would work just as well and because there is no evidence of record to indicate that the mixture of hydrogen and oxygen would work better.

Rather, Applicant’s specification teaches away from such unexpected results. Applicant teaches,

“One of several techniques can be used to provide steam to a vicinity of the insulating film. Such techniques include using a **bubbled water vapor system**, a pyrogenic system or a catalytic system, or generating steam in the chamber *in situ*.” (Emphasis added. See instant specification, page 3, lines 13-17.)

In other words, any of the presently notoriously well known means to form the steam, which are specifically used in the art for oxidation, could be used, according to Applicant. Also note that the paragraph bridging pages 7 and 8 of Applicant’s specification indicates specifically that a bubbler can be used in the instant invention.

Then the only difference is that, regarding claim 5 and further regarding claim 8, the ratio of hydrogen to oxygen is not taught.

However, each of **Emesh** and **Chivukula** indicate that the wet oxidation is carried out in water plus oxygen and ozone (**Emesh** at col. 5, lines 19-28; **Chivukula** at col. 13, lines 36-46).

“[I]n considering the disclosure of a reference, it is proper to take into account not only specific teachings of the reference but also the inferences which one skilled in the art would reasonably be expected to draw therefrom.” *In re Preda*, 401 F.2d 825, 826, 159 USPQ 342, 344 (CCPA 1968) See also *In re Lamberti*, 545 F.2d 747, 750, 192 USPQ 278, 280 (CCPA 1976). With this

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in mind, because each of **Emesh** and **Chivukula** teach that oxygen must be in excess of the water vapor, one of ordinary skill would know, based upon the stoichiometry of the reaction between hydrogen and oxygen to form the “Dryox” mixture containing water (as taught by **Van Zant**) that the ratio of hydrogen to oxygen must necessarily be less than or equal to about 0.67 because hydrogen reacts with oxygen in a 2 to 1 stoichiometric ratio ($2 \text{ H}_2 + \text{O}_2 \rightarrow 2 \text{ H}_2\text{O}$). Otherwise, the oxygen will be depleted in the formation of water and excess hydrogen would remain, contrary to the teaching in each of **Emesh** and **Chivukula**. Accordingly, one of ordinary skill would clearly recognize that using the more desirable method of “Dryox” oxidation, as taught by **Van Zant**, would necessarily require a range hydrogen to oxygen of 0.67 or less in order to achieve the mixture taught by each of **Emesh** and **Chivukula** which requires excess oxygen with the water, which overlaps the claimed ratio of 0.1 to 0.8 (instant claim 8) and 0.1 to 0.5 (instant claim 5).

Further regarding claims 2-4, although **Patel** does not recite Applicant’s exact ranges of either 450-750 °C or 750-900 °C or exact times of 20-60 seconds for the oxidation, **Patel** does disclose an overlapping temperature range of 650-850 °C and time range of 5-30 seconds, in at least one example. **Emesh** teaches 300 seconds, which is a function of the lower temperatures used. **Chivukula** teaches 30 seconds to several minutes, which are, again, temperature and material dependent. These claims are *prima facie* obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. *In re Woodruff*, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also *In re Aller*, 105 USPQ 233 (CCPA 1955) (selection of optimum ranges within prior art general conditions is obvious). It would have been obvious to one of ordinary skill in the art at the time the invention was made to optimize the temperature

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and anneal time to provide the best ferroelectric film, according to the precedent above. Also note, although **Emesh** teaches an ozone/water oxidizing temperature of 500 °C or less, **Emesh** also teaches that increasing the temperature at which the wet oxidation occurs increases the dielectric constant of the high dielectric constant film (column 8, lines 6-12) which is desired in the semiconductor device fabrication art especially for fabricating capacitors for DRAM devices. Accordingly, one of ordinary skill would be motivated to use higher temperatures than 500 °C, as suggested by **Emesh** to increase the dielectric constant of the ferroelectric layer to enable smaller capacitors to be formed which in turn enables further miniaturization of semiconductor devices using capacitors.

Regarding claim 11, **Patel** does not teach performing the ozone oxidizing or the oxygen stabilizing treatments at different temperatures, but each of **Emesh** and **Chivukula** teaches that the addition of water vapor reduces the densification/crystallization temperature from dry conditions. It would have been obvious to one of ordinary skill in the art at the time the invention was made to perform the wet ozone anneal of **Patel** in view of **Emesh** and **Chivukula** at a lower temperature than the oxygen stabilizing anneal, because each of **Emesh** and **Chivukula** teaches a lower temperature may be used for wet versus dry oxidation, and provides examples of temperatures lower than in **Patel**.

5. Claim 42 is rejected under 35 U.S.C. 103(a) as being unpatentable over **Patel** et al. (US 5,374,578) in view of either of **Emesh** et al. (US 5,728,603) and **Chivukula** et al. (US 6,066,581) and further in view of US 5,840,368 (**Ohmi**).

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The prior art of **Patel** in view of either of **Emesh** and **Chivukula**, as explained above, discloses each of the claimed features except for indicating that the steam is provided by a catalytic system.

Ohmi teaches a catalytic system for providing steam for wet oxidation. (paragraph bridging cols. 2-3 and col. 4, lines 40-45). **Ohmi** teaches that the catalytic oxidation beneficially reduces the temperature at which an oxidation may occur and provides a cleaner way of providing water (Abstract).

It would have been obvious for one of ordinary skill in the art, at the time of the invention to use the catalytic method of forming steam, taught by **Ohmi**, for the wet oxidation of **Patel** in view of either of **Emesh** and **Chivukula**, for the beneficial reasons just indicated and further because, as noted above, Applicant has not indicated that there exist anything critical to the method by which the water is formed, moreover teaching away from any criticality to such method of steam production.

6. Claim **43** is rejected under 35 U.S.C. 103(a) as being unpatentable over **Patel** et al. (US 5,374,578) in view of the excerpt from **Ghandi**, VLSI Fabrication Principles, 2nd ed. John Wiley & Sons: New York, 1994, pp. 465-466, and either of **Emesh** et al. (US 5,728,603) and **Chivukula** et al. (US 6,066,581).

The prior art of **Patel** in view of either of **Emesh** and **Chivukula**, as explained above, discloses each of the claimed features except for indicating that the steam is provided by a pyrogenic system.

Ghandi teaches the benefits of using a pyrogenic system formation of steam for oxidation indicating that the method is better than a bubbler and provides better control over the partial pressure of the water and is “well suited for the manufacturing environment.” (See paragraph bridging pp. 465-466.)

It would have been obvious for one of ordinary skill in the art, at the time of the invention to use the pyrogenic method of forming steam, taught by **Ghandi**, for the wet oxidation of **Patel** in view of either of **Emesh** and **Chivukula**, for the beneficial reasons just indicated and further because, as noted above, Applicant has not indicated that there exist anything critical to the method by which the water is formed, moreover teaching away from any criticality to such method of steam production.

7. Claim **44** is rejected under 35 U.S.C. 103(a) as being unpatentable over **Patel** et al. (US 5,374,578) in view of either of **Emesh** et al. (US 5,728,603) and **Chivukula** et al. (US 6,066,581).

The prior art of **Patel** in view of either of **Emesh** and **Chivukula**, as explained above, discloses each of the claimed features of claim 44. Additionally both **Emesh** and **Chivukula** teach that water is provided by a bubbler system (**Emesh** at col. 5, lines 57-59; **Chivukula** at col. 13, lines 40-46).

It would have been obvious for one of ordinary skill in the art, at the time of the invention to also use the bubbler for the wet oxidation, already indicated as obvious over either of **Emesh** and **Chivukula**, for the oxidation of **Patel**, because this is the manner in which **Emesh** and **Chivukula** provide water vapor and since one of ordinary skill would be motivated to use water

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vapor, for the reasons indicated earlier, one of ordinary skill would be especially motivated to use the system taught in **Emesh** and **Chivukula** to provide the water vapor.

Response to Arguments

8. Applicant's arguments filed 3/27/01 have been fully considered but they are not persuasive.

Applicant argues

“First, not all claim limitations are taught or suggested by the prior art, either alone or in combination. None of Patel, [Van] Zant, Emesh or Chivukula teach or suggest the step of ‘*subjecting the dielectric film to a heat treatment in an ambient comprising a stabilizing gas selected from the group consisting of N₂, O₂, O₃, NO, and N₂O*’ **after** the ‘wet oxidation with steam provided by heating a mixture of hydrogen and oxygen in a rapid thermal process chamber ... wherein *the ratio of the hydrogen to oxygen gases in the mixture is in the range of about 0.1 to 0.8*,’ as independent amended claim 8 recites.” (Italicized emphasis in original. Bold emphasis added.)

Examiner respectfully disagrees for the reasons indicated in the rejection of the amended claim 8 and further because Applicant does not claim the sequence of steps, as presently argued. Rather, dependent claim 10 expressly claims that the anneal in the stabilizing gas occurs **before** the wet oxidation, contrary to the present argument. Assuming, *arguendo*, that the sequence were as presently argued, then claims 10 and 8 would contradict each other creating an method lacking enablement, because the steps could not be performed in two different sequences simultaneously. Moreover, Applicant clearly admits that the sequence is inconsequential, as either may be used. Examiner also notes that the “stabilizing gas” has been defined as, *inter alia*, O₂ or O₃ in the claim. Patel clear discloses separate anneals in O₂ and O₃, which is by applicant’s own definition a stabilizing gas. Accordingly, one such anneal is the “anneal in the stabilizing gas” which

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Applicant alleges is absent. The ratio of hydrogen to oxygen is obvious for the reasons indicated above.

Applicant argues that Patel would not be properly combined with either of Chivukula and Emesh because Patel, allegedly teaches away from the use of oxygen. Examiner respectfully but emphatically disagrees because the express teaching of Patel indicates that **oxygen**, ozone, or **air** may be used to anneal the ferroelectric (column 4, lines 10-11). Patel further discloses express examples, wherein **oxygen alone** or oxygen-ozone combination anneals are used (column 4, lines 23-35). To allege that Patel teaches away from the use of oxygen simply because ozone is “preferred” in one exemplary embodiment, is simply false based upon the express teachings of Patel. It simply does not make sense to say that oxygen should not be used and then expressly use it time and time again in the several examples indicated in Patel. For at least this reason, Applicant’s argument lacks merit for ignoring the express teachings of Patel and further for not considering the reference as a whole.

Applicant’s arguments regarding the combination of Van Zant with Patel in view of either of Emesh or Chivukula are also considered to be in error for the reasons indicated in the rejection, most specifically that combustion of hydrogen and oxygen is far cleaner and preferred to a bubbler.

Conclusion

Any inquiry concerning this communication from examiner should be directed to Erik Kielin whose telephone number is (703) 306-5980 and e-mail address is erik.kielin@uspto.gov.


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The examiner can normally be reached by telephone on Monday through Thursday 9:00 AM until 7:30 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Olik Chaudhuri, can be reached at (703) 306-2794 or by e-mail at olik.chaudhuri@uspto.gov. The fax phone numbers for the organization where this application or proceeding is assigned are 703-872-9318 for regular communications and 703-872-9319 for After Final communications.


EK

August 1, 2002


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